Indian J. Phys. **49**, 477–481 (1975)

Dense gas formulation of molten alkali halides equilibrium properties

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(*Received* 30 *December* 1974, *revised* 21 *March* 1975)

The concepts of dense gas formulation have been applied to calculate the thermodynamic equilibrium properties namely the thermal expansion coefficient, compressibility and velocity of sound at melting point to another class of system namely the molten alkali halides. Semiquantitative agreement with the experimental data gives us more confidence in these simple concepts.

1. Introduction

It has become increasingly evident that the hard sphere fluid (Smith & Alder 1959, Alder & Wainwright 1963) may be considered as a reasonable limit case for the description of the liquid state. The physical basis, substantiated by the molecular dynamic calculation (Paskin 1967), for this is the reality that the liquid structure is insensitive to the detailed pairwise interaction, and the structures of all the metallic and nonmetallic simple liquids may be considered approximately the same at their melting point. The success of the Percus—Yevick hard sphere equation has led to its widespread use in the numerical calculation of the equilibrium (Ascarelli 1968, Takeuchi 1973) and transport properties (Ascarelli & Paskin 1968, Sharma 1968) of rare gas liquids, liquid metals near the melting point. More recently (Ascarelli & Harrison 1969, Hasegawa & Watabe 1972), the importance was mentioned of the structure independence cohesion term E_0 in the description of compressibility of liquid metals. Such a simplified model led Shimoji (Takeuchi 1973) to calculate the thermodynamic properties of liquid metals and recently Turner *et al* (1973) to calculate the partial structure factors as a function of concentration in liquid alloys with a qualitative agreement. It is to be noted that this picture is consistent with the Van der Waals concept (Young & Alder 1971) of a fluid which emphasizes the fact that the particles have a potential made up of a hard core plus a weak long range attractive force.

The generally successfully predictions of the dense gas formulation for metal- and the rare gases suggest that these concepts should be applied to another class of substances namely the ionic salts. It has to be noticed that these physical arguments are not strictly true (Woodcock & Singer 1971) for molten

salts. The justification of such a calculation for molten ionic salts lies in the fact that Young & Alder have applied the concept of hard sphere molecule (diatomic) with the packing fraction, at melting point, $\eta = 0.45$, to have the value of critical constant ratio $P_c V_c/RT_c$, in reasonable agreement with the experiment. Therefore, the motivation of this work is twofold. Firstly, the calculation is used to demonstrate the importance of properly identifying the pseudomolecular species which might exist much below the critical point (Young & Alder 1971). Secondly, the comparison of the calculated values of the thermodynamic properties namely the thermal expansion coefficient and the compressibility with the experimental results may suggest the extent of improvement which may come from the long range interatomic interactions present in molten salts.

2. Model

We consider the system of interest as a molecular one component system (Berne & Rice 1964). The diatomic molecule has been taken as the molecular unit which has to be treated as a hard sphere pseudomolecule. These basic entities i.e., neutral pseudomolecules can be thought essentially as free particles immersed in a uniform potential which will provide the cohesion that the hard sphere gas otherwise lacks. With this picture in mind we can write down the total binding energy E (per molecule) of the system as

$$NE = \tfrac{1}{2} \sum_{i,j\ (i \neq j)} V(r_{i,j}) + NE_0, \qquad \ldots (1)$$

where N is the number of molecules in the system. Having recognized the prevailing role of the short range repulsive intermolecular forces in determining the structure of simple liquid system we feel justified in approximating the effective pair interaction $V(r)$ by a simple hard-sphere potential. This is positive and infinite for distance less than 2σ and zero otherwise. We consider σ as an approximate measure of the radius of a pseudo molecule. E_0 represents the cohesive energy that is responsible for supplying the cohesion to the hard-sphere system, without changing the equilibrium configuration of the particles.

We approximate for simplification, E_0 by $-B/V^{1/3}$ which contains the energy of interaction among the molecules and assume it to be independent of their positions. B is a constant which is to be determined and for simplicity is written in terms of a dimensionless constant A defined by $B = 3A V_m^{1/3} kT_m$. V is the molecular volume of the system, the subscript m corresponds to the melting point.

We then write the pressure of the system as

$$\frac{PV}{NkT} = \frac{P_h V}{NkT} - A\left(\frac{V_m}{V}\right)^{1/3} \frac{kT_m}{kT}. \qquad \ldots (2)$$

Here N is the number of molecules in the system, k is the Boltzmann constant, T is the temperature (°K). P is the total pressure, P_h corresponds to the pressure of a hard-sphere system which is given by the equation of state (Carnahan & Starling 1969)

$$\frac{P_h V}{NkT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \qquad \ldots (3)$$

where η is the packing fraction defined by $\eta = (4/3)\pi\sigma^3 N/V$ with σ as the hard-sphere radius which is expected to be temperature dependent.

We assume, following the work of Young & Alder (1971), for the alkali halides that at melting point the packing fraction is nearly equal to 0.45 and its temperature variation at constant volume is given by (Ascarelli 1968)

$$\frac{1+\eta_v+\eta_v^2-\eta_v^3}{(1-\eta_v)^3} = 3.7+5.7\,\frac{T_m}{T}, \qquad \ldots (4)$$

where η_v is the packing fraction at constant volume. This gives the variation of η_v with T. Further, assuming the equivalence of repulsive and attractive contributions at T_m under the normal conditions

$$A = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} = 9.4.$$

Having interpreted the various parameters to be used in the dense gas formulation we can write down from eq. (2), the equations for thermal pressure coefficient

$$\gamma_v = nk\left[\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} + \frac{2(2+2\eta-\eta^2)}{(1-\eta)^4}\cdot T\cdot\frac{d\eta}{dT}\right], \qquad \ldots (5)$$

and for thermal expansion coefficient

$$\alpha_p = \frac{1}{T}\,\frac{1+\dfrac{2(2+2\eta-\eta^2)}{1+\eta^4}\cdot T\cdot\dfrac{d\eta}{dT}}{\dfrac{(1+2\eta)^2+\eta^3(\eta-4)}{1+\eta^4}-\dfrac{4}{3}}. \qquad \ldots (6)$$

The isothermal compressibility is given by

$$\chi_T = \left[nkT\left\{\frac{(1+2\eta)^2+\eta^3(\eta-4)}{(1-\eta)^4}-\frac{4}{3}\,\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right\}\right]^{-1}, \qquad \ldots (7)$$

which is related with the velocity of sound (v_s) by the expression

$$\rho v_s^2 = \frac{1}{\chi_s}, \qquad \ldots (8)$$

where n is the number density ($n = N/V$), ρ is the mass density ($\rho = mn$) and χ_s is the adiabatic compressibility given by $\chi_T = \frac{c_p}{c_v}\chi_s$. χ_T is related with the structure factor $S(0)$ in the long wave limit by

$$S(0) = nkT\chi_T. \qquad \ldots (9)$$

3. Results and Discussion

In table 1, we compare the calculated values of thermal expansion coefficient, compressibility and velocity of sound at T_m with experimental data (Janz 1967). In the calculation of α, we have taken the value of variation of η with T i.e., $d\eta/dT$ as the average of $d\eta_v/dT$ ($= 1/15\ T_m$) from eq. (4). In order to calculate the values of the velocity of sound we assume to a good approximation that $c_p/c_v = 1.33$ for all the alkali halides except the chlorides for which the data are available. The temperature variation of reduced compressibility

$$\chi_r = \frac{\chi_T(T)}{\chi_T(T_m)}$$

with the reduced temperature $T_r = T/T_m$ is also seen to be such that the calculated values of χ_r/T_r was 1.1 which was in reasonable agreement with the experimental value 0.9.

Table 1. Comparison of the calculated and experimental value of the thermal expansion coefficient, compressibility and velocity of sound of molten alkali halides at T_m. The experimental data are taken from the Molten Salt Handbook (Janz 1967).

System	T_m (°K)	$\alpha_p \times 10^4$ (deg^{-1})		$\chi_T \times 10^{12}$ (cm^2/dyne)		v_S (M/sec.)	
		Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
LiCl	883	4.06	2.87	16.74	19.3	2232	2556
LiBr	823	4.36	2.59	21.48	21.4	1566	1800
NaCl	1073	3.34	3.49	18.06	28.7	2220	2483
NaBr	1020	3.51	3.50	22.22	31.4	1603	1798
NaI	933	3.84	3.48	30.05	37.3	1270	1502
KCl	1043	3.44	3.84	24.05	35.6	1902	2275
KBr	1007	3.57	3.91	28.53	39.1	1480	1770
KI	954	3.76	3.89	36.64	48.2	1220	1555
CsCl	918	3.90	3.84	33.70	39.0	1251	1597

It is really instructive to see that the simple picture of hard-spheres in a uniform background potential is able to describe semi-quantitatively the thermal expansion coefficient, compressibility and velocity of sound at the melting temperature in molten alkali halides of widely different masses, densities and melting

points. Thermal expansion coefficient does not seem to be very sensitive to the details of the interatomic potential. However, in LiCl and LiBr the calculated α values are very much different from the experimental ones, which is not unexpected. This difference may be attributed to the small size of Li ions in the real system. The experimental values of χ_T and v_s are uniformly higher than the theoretical results. It is expected to be due to the proper long range interactions (Woodcock & Singer 1971) which is present in molten halides and has not been considered in the present analysis. In view of this, substantial improvement of these concepts will be required so as to incorporate, reasonably, the interatomic potential in alkali halides as a function of density and temperature.

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